SEPARATION, CHARACTERIZATION AND LIGAND EXCHANGE STUDIES OF μ-SULPHATO DI-CHROMIUM COMPLEXES

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Abstract—The cationic complexes of 33% basic chromium sulphate have been separated by ion-exchange chromatography using a combination of cerous perchlorate and ammonium perchlorate as eluting agent. Two of the complexes have been identified as μ-dihydroxo, μ-sulphato, hexa aquo di-chromium species and μ-oxo, μ-sulphato, octa aquo di-chromium species. The kinetics of the isotopic sulphate exchange between the ionic sulphate and sulphato ligand of the complex have been measured and a mechanism for the exchange has been proposed.

INTRODUCTION

THIRTY-THREE per cent basic chromium sulphate solution is an important tanning agent for crosslinking and stabilising the collagenous protein of hide. It contains several complexes whose compositions are unknown. A knowledge of the nature and characteristics of these individual complexes is essential for an understanding of the mechanism of tanning. With this end in view, an attempt has been made to separate and characterise the different complexes present in the chrome tanning solution.

Ion-exchange chromatography has been extensively used in the separation of coordination complexes[1]. In acidic chromium sulphate solutions, the different complexes have been separated by elution with increasing concentrations of perchloric acid[2, 3]. Plane et al.[4, 5] have used a combination of lanthanum perchlorate and perchloric acid as eluting agent to separate the products of oxidation of chrome solutions with molecular oxygen and also the species present in the boiled chromic perchlorate solutions. The complexes present in basic chromium sulphate have been separated using perchloric acid as eluting agent[6].

Recently Kuntzel and Mahdi[7] have reported the detection and separation of complexes in chromium sulphate solutions using paper and ion-exchange chromatography. The fractions were separated on a sephadex SEC column using sodium chloride and hydrochloric acid as eluting agents.

Although perchloric acid has been used to separate the complexes, its use to separate basic chromium complexes has limitations since it is well known that

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mononuclear hydroxy species of chromium react with acids [8] and the binuclear species with bridged hydroxyl groups undergo cleavage reactions [9]. Cerium salts have also been used as eluting agents; Finholt et al.[10] separated a mixture of basic sulphato chromium species by means of cerous perchlorate and identified one bichromium species. Very recently Gutlich et al.[11] have developed a separation technique for the various chrome complexes formed by the neutron irradiation of potassium chromate, using sodium perchlorate and lanthanum perchlorates as eluting agents. Cady and Connick [12] have eluted the different ruthenium species using cerous perchlorate containing perchloric acid. In the present study, to avoid complications due to the acid, a mixture of cerous perchlorate and ammonium perchlorate has been used.

Two of the complexes separated have been shown to be binuclear chromium species bridged by sulphate. It is of considerable interest to study the kinetics of $^{35}SO_4$ exchange with such sulphate-bridged complexes. Isotopic sulphate exchange with basic chromium sulphate solution containing the mixture of complexes has been reported [13, 14].

EXPERIMENTAL

Reagents

Thirty-three per cent basic chromium sulphate solution was prepared by reducing chromic oxide (Analar) with 100 vol. hydrogen peroxide in the presence of the calculated amount of sulphuric acid. The excess of peroxide was removed by heating the solution on a water bath.

Mixed rare earth oxides (Indian Rare Earths Ltd) containing predominantly cerium oxide were heated with 2M perchloric acid and hydrogen peroxide was added to reduce ceric. The pH of the solution was adjusted to 3·0 and cerium was estimated gravimetrically by precipitation as the oxalate and ignition to ceric oxide [15].

Dowex 50 W − X 12(100–200 mesh) was purified by warming with alkaline peroxide and later converted into NH_4^+ form by equilibrating with 1 M ammonium nitrate solution and then on passing excess of ammonium nitrate through the resin. The pH of the resin was adjusted to 3·0.

^{35}S was supplied by the Bhabha Atomic Research Centre, Trombay, as sulphuric acid in dilute hydrochloric acid.

Separation of the complexes

Four g of resin were placed in a column of 12 cm length and 0·8 cm i.d. ice cold water was circulated through an outer jacket to maintain the temperature of the resin below 5°C. 5 ml of the 33% chromium sulphate solution (0·45 M) were passed through the column and the flow rate was adjusted to 0·4 ml/min. The non-cationic fraction was first removed by passing water adjusted to pH 3·0 with perchloric acid. A dark green band of 3 cm length was observed at the top of the column and a light green band of 4–5 cm length at the bottom. Optimum concentrations of the cerous perchlorate/ammonium perchlorate eluting solutions were obtained by varying the concentrations and observing separations of the bands. 40 ml of 0·05 M cerous perchlorate containing 0·5 M ammonium perchlorate were passed through the column eluted the lower light green band completely. A dark green band started moving down and reached the bottom of the column when 15 ml of this solution were passed. Another dark green band

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started moving downward and was about 2 cm from the bottom of the column when the entire 40 ml were passed. At this stage, circulation of ice cold water was stopped and a mixture of 0·05 M cerous perchlorate and 1·5 M ammonium perchlorate was passed. The third green band was also eluted completely, leaving behind the violet hexa aquo chromium species at the bottom of the column. Samples from the central portions of the three bands were collected, and will be referred to as the I, II and III complexes. The last portion of the third band contained cerous perchlorate and was rejected.

Tracer experiments

To study the kinetics of exchange with $^{35}SO_4$, the complex solutions of the desired concentrations (ionic strength adjusted to 1·0 with ammonium perchlorate) in polythene bottles were kept in a thermostat at $25° \pm 0·2°C$, for 1 hr before the addition of the isotope. Isotope exchange was initiated by injecting ^{35}S and shaking the solution. The progress of the reaction was followed by removing aliquots at different time intervals and measuring the decrease in the activity of ionic sulphate precipitated as benzidine sulphate. To obtain sufficient precipitate to give an "infinitely thick" layer, 25 mg of carrier sulphate were added to the aliquots. The precipitate was separated by centrifugation, washed twice with cold distilled water, once with acetone and filtered using a filter assembly [16] suitable for counting. The precipitates after drying with acetone and ether were counted for ^{35}S activity using a G.M. counter.

RESULTS AND DISCUSSION

Besides the hexa aquo chromic species, three complexes have been eluted. Finholt *et al.*[10] separated two complexes only from the ion-exchange column below hexa aquo chromic species, probably owing to the differences in conditions of elution.

Characterization of the complexes

The complexes could not be crystallised, so the studies for the assignment of formulae and structures had to be carried out with concentrated solutions. To obtain larger samples, six bigger columns (25 × 1 cm) were used simultaneously and the separated complexes were concentrated in a vacuum oven at low temperature. The ammonium perchlorate present was partially removed by dialysis at low temperature using the Visking tube. The complexes were purified by re-absorbing from dilute solution on a small ion-exchange column and re-eluting with the appropriate eluting agent. This process was repeated until pure species were obtained. The purity of each complex was judged by the formation of single band after reabsorbtion on the small ion-exchange column and by its elution behaviour. Absorption spectra, could not be used for this purpose because the spectra of two of the complexes do not differ significantly.

Chemical composition of the species

The chromium concentration was determined by oxidising to chromate with alkaline peroxide and measuring the chromate absorbance at 372 mμ[17]. The sulphate was determined gravimetrically as barium sulphate. The Cr/SO$_4$ ratios obtained for the I, II and III complexes were 1·00:1, 2·02:1 and 2·01:1, respectively.

Figure 1 shows the visible absorption spectra of the three complexes. The spectrum for the I complex with $E_{max(585)} = 19·8$ and $E_{max(418)} = 20·7$ agrees with

16. G. R. Choppin, *Experimental Nuclear Chemistry*, p. 71. Prentice Hall, Englewood Cliffs, N.J (1961).
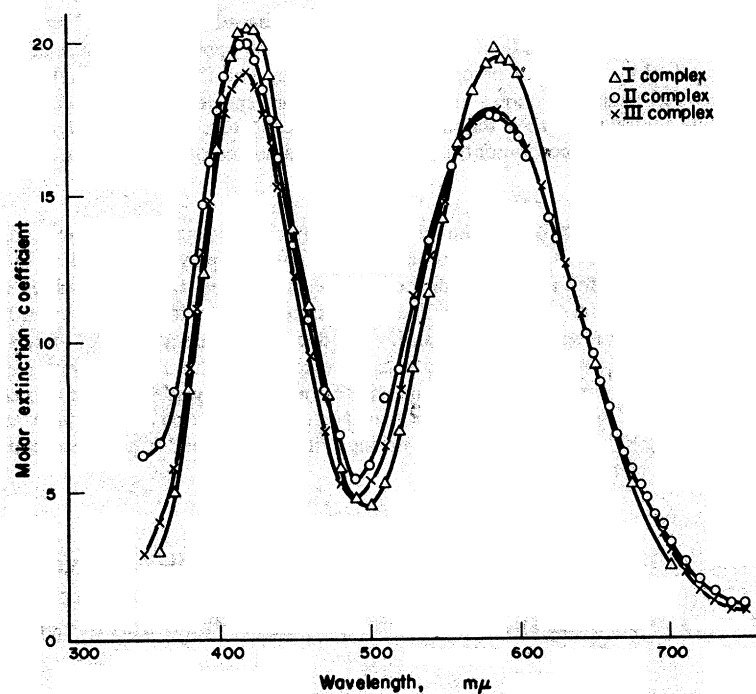17. G. W. Haupt, *J. Res. natn. Bur. Stand.* 48, 414 (1952).

Fig. 1. Visible spectra of the complexes.

that of the monosulphato penta aquo chromium species reported previously [2, 3, 18].

The charge per Cr atom and the charge per entire chromium species were determined for the II and III complexes to establish whether the complexes are mononuclear or binuclear. The procedure adopted by Connick and Cady [11] for the charge determination of ruthenium species was followed. Ten ml of the concentrated and purified complex solutions were passed through ion-exchange columns containing 2 g of resin in the NH_4^+ form maintained at low temperature, the columns were then rinsed with ice cold water. The displaced NH_4^+ ions were collected and the NH_4 content in the initial and final solutions were determined by micro Kjeldahl method. The Cr content of the solution was determined by oxidising to chromate and measuring the absorbance at 372 $m\mu$. From the Cr content in the solution and the equivalents of NH_4^+ displaced, the charge per Cr atom was calculated; the values are given in Table 1.

Charge per species

The charge per species was also determined following the method of Cady and Connick [12], based on the dependence of the equilibrium distribution of the unknown charged ion, on the concentration of the known charged exchangeable ion, in the resin and aqueous phase. The complexes of known concentration were equilibrated for 1 hr with two different concentrations of ammonium perchlorate,

18. K. M. Jones and J. Bjerrum, *Acta chem. scand.* **10**, 974 (1965).

Table 1

No.	Species	Cr content (g atom)	NH₄⁺ content displaced. Difference in initial and final NH₄ content (atom)	Charge/Cr atom
1	II Complex	5.125×10^{-4}	4.973×10^{-4}	0.97
2	II Complex	4.683×10^{-4}	4.831×10^{-4}	1.03
3	III Complex	2.342×10^{-4}	2.462×10^{-4}	1.05
4	III Complex	5.825×10^{-4}	6.99×10^{-4}	1.02

in the presence of Dowex 50W-X12(100–200 mesh) in the NH₄⁺ form and the chromium concentration in the solutions after equilibration were determined. Table 2 contains the results for the II and III complexes; these were substituted in the equation

$$\frac{\overline{(M_1^{b+})}(NH_4^+)_1^b}{(M_1^{b+})\overline{(NH_4^+)_1^b}} = \frac{\overline{(M_2^{b+})}(NH_4^+)_2^b}{(M_2^{b+})\overline{(NH_4^+)_2^b}}$$

where the bar represents the concentration in the resin phase of the complex M of charge b in the 1 and 2 equilibration with different NH₄ concentrations. The chrome content in the resin phase was calculated from the difference between the known amount of chromium taken and the chromium content left in the solution after the equilibration. The exchange capacity of the resin was determined to be 3·3 meq/gm of the resin and since a known amount of the resin was taken the NH₄⁺ content in the resin taken initially was known. Since the chromium content in the resin phase was calculated and the charge of the chromium complex was determined separately, the ammonium content displaced from the resin was calculated. The difference between the ammonium content taken initially and the amount displaced by chromium gave the ammonium content in the resin phase after equilibration. Correction was made for the ammonium concentration in solution after equilibration for the ammonium ions displaced from the resin. Since the charge per species value cannot be a fraction, the values of 1·74 and

Table 2. Charge per species of the complexes. Weight of resin = 0·5 g

| No.	Species	Total Cr content taken for equilibration (g atoms)	Strength of NH₄ClO₄ taken for equilibration (M)	Vol of NH₄ClO₄ (ml)	Cr conc. in sol. after equilibration (g atoms/l)	Charge per species
1.	II Complex	3.18×10^{-5}	0·5	30	6.9×10^{-4}	1·74
		3.18×10^{-5}	0·25	60	2.8×10^{-4}	
2.	II Complex	2.175×10^{-5}	1·08	30	1.2×10^{-4}	1·75
		2.175×10^{-5}	0·54	60	4.445×10^{-5}	
3.	III Complex	4.55×10^{-5}	0·5	20	1.32×10^{-3}	1·75
		4.55×10^{-5}	0·25	40	0.515×10^{-3}	
4.	III Complex	4.375×10^{-5}	0·6	30	4.275×10^{-4}	1·74
		4.375×10^{-5}	0·3	60	1.45×10^{-4}	
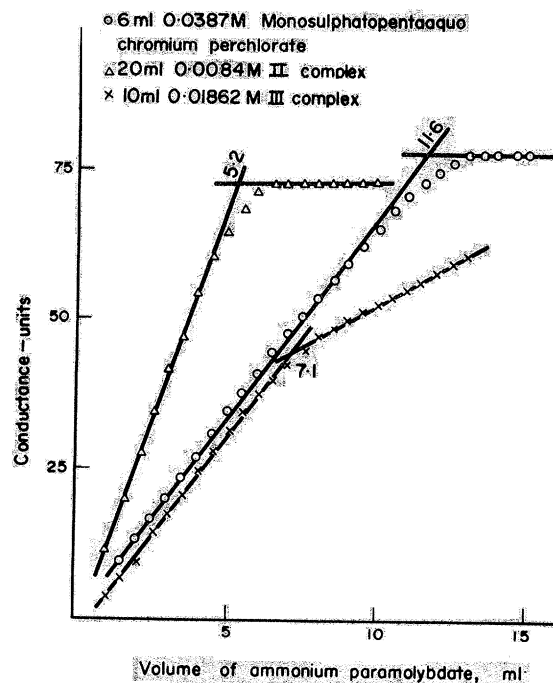
Fig. 3. High frequency conductometric titrations for the complexes with 0·1 M ammonium paramolybdate.

Fialkov *et al.*[13] obtained a complex exchange curve for 33% basic chromium sulphate due to the presence of more than one sulphato complex. For zero per cent basic chromium sulphate which was later shown by Finholt *et al.*[3] to contain the monosulphato pentaaquo chromium complex with monodentate sulphate, the $t_{1/2}$ values for exchange even at 20°C are of the order of 20 hr. The
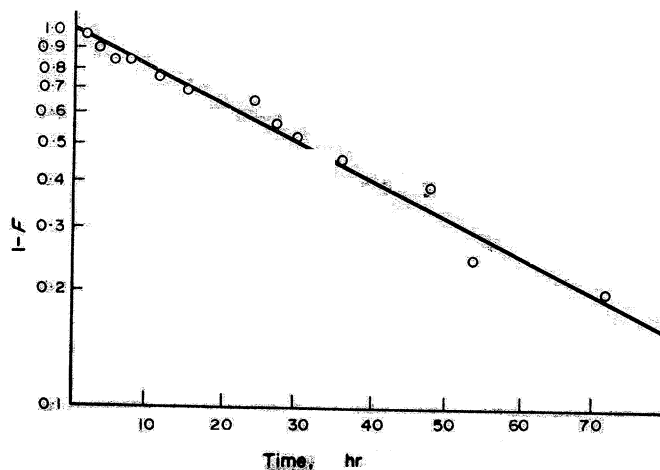

Fig. 4. McKay plot for the II complex at 25°C.

half times for the bidentate sulphate complexes, encountered in the present study, of the order of 30 hr at 25°C, reflects the slowness in the exchange rate for the bidentate sulphate ligand.

Exchange experiments were carried out at 25°C with varying ionic sulphate concentration, ligand sulphate concentration and pH. Table 3 gives the results

Table 3. Exchange data for the μ-sulphato μ-di-hydroxo complex at different concentrations of ionic sulphate and ligand sulphate. Temperature = 25°C; pH = 2·4; ionic strength = 1·0 M

No.	(a) Ligand sulphate concentration (M)	(b) Ionic sulphate concentration (M)	$t_{1/2}$ (hr)	$R = \dfrac{0.693}{t_{1/2}} \dfrac{ab}{(a+b)}$ (moles. l^{-1}. m^{-1})
1	0·00167	0·001	29·5	2.45×10^{-7}
2	0·00295	0·001	29	2.97×10^{-7}
3	0·004375	0·001	31·5	2.98×10^{-7}
4	0·004375	0·0025	30	6.13×10^{-7}
5	0·00425	0·005	29	9.15×10^{-7}

for the μ-sulphato μ-dihydroxo chromium complex at varying ionic sulphate and ligand sulphate concentrations and the last column gives R, the rate of isotopic exchange. The rate of exchange/ligand sulphate concentration was found to increase linearly with an increase in the ionic sulphate concentration, at a fixed ligand sulphate concentration. The experimental values of R, obtained in the range of conditions can be correlated by the equation

$$R = k_1 \text{ ligand sulphate} + k_2 \text{ (ligand sulphate)(ionic sulphate)}$$

where k_1 and k_2 are the rate constants which may be evaluated from the plot of R/ligand sulphate concentration vs ionic sulphate concentration. Table 4 gives the results for the two complexes at varying pH values. For a particular complex, since the ligand sulphate concentration is almost a constant and ionic sulphate

Table 4. Exchange data for the complexes at different pH values. Temperature = 25°C; ionic strength = 1·0 M

No.	Species	Ligand sulphate concentration (M)	Ionic sulphate concentration	pH	$t_{1/2}$ (hr)
1	μ-sulphato-μ-dihydroxo complex	0·003725	No added sulphate	2·0	48·0
2	μ-sulphato-μ-dihydroxo complex	0·00375	No added sulphate	2·8	17·5
3	μ-sulphato-μ-dihydroxo complex	0·00405	No added sulphate	3·3	6·75
4	μ-sulphato-μ-oxo complex	0·004825	No added sulphate	2·0	44·0
5	μ-sulphato-μ-oxo complex	0·00475	No added sulphate	2·8	16·0
6	μ-sulphato-μ-oxo complex	0·005025	No added sulphate	3·3	6·5